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IN MIXED VALENCE SYSTEMS

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INTERSITE INTERACTIONS AND SUSCEPTIBILITY IN MIXED VALENCE SYSTEMS *

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ABSTRACT

This paper considers the effect of intersite processes on the susceptibility in mixed valence system. The method of thermodynamical perturbation used in this paper can also be generalized to study other properties of mixed valence system. The general formula of partition function of two-site interactions for the mixed valence system is given. The numerical calculations show that the intersite interaction is large enough to explain the minimum of susceptibility discovered in experiments. The different types of our theoretical curves predict that the susceptibility should exhibit a rich variety of behaviour at low temperature for various materials.

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I. Introduction

The problem concerning the role of interactions between f electrons located at different lattice sites in mixed valence systems has attracted considerable attention in recent years.¹⁻⁵ Part of the reason is the importance of seeking the mechanism of superconductivity in heavy fermion materials. In a mixed valence system where two different configurations of f electrons have nearly equal energies, the dynamic and thermodynamic properties of mixed-valence substances differ strikingly from the corresponding properties of non-mixed valence materials. The intersite interactions in mixed valence system have been emphasized to be much stronger than that in non-mixed valence system as well.⁶

However, most of theoretical works on the thermodynamic properties have dealt only with the on-site processes.^{1,2} In spite of some apparent successes of these calculations there remain some doubt whether it is allowed to neglect the effect of intersite processes. For example, the phenomena of appearing minimum of low-temperature susceptibility can not be interpreted by the on-site results obtained by Bringer and Lustfeld,¹ Ramakrishnan² et al. The obvious discrepancies between the experimental and theoretical on-site results at low temperatures thus strongly suggest that interactions between different sites should play an important role at low temperatures.¹ For the purpose to understand ^{the} above low temperature thermodynamic properties, more information about the range of intersite correlations are greatly needed.

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In the present paper we are motivated to derive the form of intersite interactions by using the thermodynamic perturbation theory for systems with strong local correlations,³ then we calculate the susceptibility of intersite interactions for mixed valence system. The properties of various terms in the intersite interactions are analysed and the phenomena of appearing susceptibility minimum at low temperatures⁴ can be attributed to the effects of intersite interactions.

The organization of the paper is as follows: In Sec. II we derive the form of intersite interactions by using the perturbation expansion technique developed by Keiter and Grewe.³ Sec. III calculate numerically the temperature dependences of the susceptibility and then use our results to analyse some available experiment phenomena. Finally, in Sec. IV we make some discussions.

II. Theoretical Formalisms

The intermediate valence system is comprised of two sets of electronic states: a periodic array of localized, strongly correlated, f states and the set of itinerant band states. These states interact in a way such that the electrons may be transferred between the two types of states. The Hamiltonian governing the system can be conveniently written down by using the transfer-operators $X_{mm'}^{(V)}$ introduced by Hubbard³

$$H = \sum_{\vec{R}\sigma} \epsilon_{\vec{R}\sigma} d_{\vec{R}\sigma}^{\dagger} d_{\vec{R}\sigma} + \sum_{\nu, M} E_M X_{MM}^{(V)} + \sum_{\nu, \vec{R}\sigma} \sum_{MM'} [N_S^{-1/2} e^{i\vec{k}\cdot\vec{R}\nu} v_{\vec{R}}(\sigma MM') d_{\vec{R}\sigma}^{\dagger} X_{MM'}^{(V)} + H.c.] \quad (1)$$

where $d_{\vec{R}}$ and $d_{\vec{R}}^{\dagger}$ are respectively, destruction and creation operators of an electron with spin σ in the state labeled by the Bloch wave vector \vec{k} , $v_{\vec{R}}(\sigma MM')$ is the appropriate hybridization matrix element, N_S the number of sites.

We restrict ourselves to mixed-valent substances in which one of the two different occupation of the f-shell is non-magnetic, while the other has an angular momentum J and its z-component M . All energies are those of excitations with respect to the chemical potential μ and include the magnetic field splitting:

$$\epsilon_{\vec{R}\sigma} = \epsilon_{\vec{R}} - \frac{1}{2} g \mu_B \sigma B \quad (2)$$

$$E_{M_0} = E_{n_0} \quad (3)$$

$$E_{M_1} = E_{n_0+1} - g \mu_B M B \quad (4)$$

Difficulties arise in treating the hybridization (last term in Eq.(1)) by a perturbation technique since the transfer-operators $X_{MM'}^{(V)}$ do not obey simple Boson- or Fermion-commutation relations and Wick's theorem does not hold due to the many-body nature of the unperturbed Hamiltonian. Using a mixed Goldstone-Feynman diagram expansion technique as developed by Keiter and Grewe,³ the general structure of the partition function can be written as follows:

$$\frac{Z}{Z_0} = 1 + \sum_i S_i + \sum_{\{i,j\}} (S_i S_j + S_{ij}) + \dots \quad (5)$$

where S_i is the sum of all single site processes at site i , and S_{ij} the sum of all processes involving two sites i and j , S_{ijk} the one involving three sites etc. Without the intersite contributions, Z/Z_0 is just a product of single site contributions

$$\frac{Z^{SS}}{Z_0} = 1 + \sum_i S_i + \sum_{\{ij\}} S_i S_j + \dots = \exp \left[\sum_i \ln(1+S_i) \right] \quad (6)$$

With the aid of Eq. (6) we may write:

$$\frac{Z}{Z_0} = \frac{Z^{SS}}{Z_0} \left(1 + \sum_{\{ij\}} \widehat{S}_{ij} + \sum_{\{ij,kl\}} \widehat{S}_{ij} \widehat{S}_{kl} + \dots \right) \quad (7)$$

Here

$$\widehat{S}_{ij} = S_{ij} / (1+S_i)(1+S_j) \quad (8)$$

etc.

Analogous to the single site case, the correction due to two sites for the partition function can be obtained by means of excluded-site cumulant expansion

$$\begin{aligned} Z^{TS} &= 1 + \sum_{ij} \widehat{S}_{ij} + \sum_{\{ij\} < \{kl\}} \widehat{S}_{ij} \widehat{S}_{kl} + \dots \\ &= \exp \left[\sum_{ij} \widehat{S}_{ij} \right] \end{aligned} \quad (9)$$

Indirect interactions between the f electrons at different sites via band electrons are generated. A f electron can be mixed into the band at a site i , propagate and then be mixed into the f shell at a different site j . The first and last step both involve a factor $|v_R(\sigma M M')|^2$ so that the intersite interaction between the f orbitals, mediated by the band states, is of at least fourth order in the hybridization.

A corresponding diagram of two site process is shown in Fig. 1. Appropriate diagram rules can be found in the work of Keiter and Grewe.³

With the consideration of the two-site processes as shown in Fig. 2, partial summations of their contributions can be worked out. Denoting the simplest intersite processes (Fig. 1) for the partition function by C_{ij} , the contribution is of the form:

$$S_{ij} = C_{ij} (1+S_i)(1+S_j) \quad (10)$$

The expression of C_{ij} can be written out straightforwardly by generalizing the diagrammatic techniques of Keiter and Grewe.³ Two f -Green's functions at each site connected by two band Green's functions exist in C_{ij} :

$$\begin{aligned} C_{ij} &= - \sum_n \sum_{M_0 M_1} \sum_{M'_0 M'_1} G_{M_0 M_1; M'_0 M'_1}(\vec{R}_{ij}, i\omega_n) G_{M'_0 M'_1; M_0 M_1}(-\vec{R}_{ij}, i\omega_n) \\ &\quad \times F_{M_0 M_1; M_1 M_0}(i\omega_n) F_{M'_0 M'_1; M'_1 M'_0}(i\omega_n) \end{aligned} \quad (11)$$

where $G_{M_0 M_1; M'_0 M'_1}(i\omega_n)$ is the band Green's function weighted by the hybridization matrix elements

$$G_{M_0 M_1; M'_0 M'_1}(\vec{R}_{ij}, i\omega_n) = N_S^{-1} \sum_{\vec{k}} v_{\vec{k}}(\sigma M_0 M_1) v_{\vec{k}}^*(\sigma M'_0 M'_1) e^{i\vec{k} \cdot \vec{R}_{ij}} \frac{1}{i\omega_n - \epsilon_{\vec{k}\sigma}} \quad (12)$$

$\omega_n = (2n+1)\pi/\beta$ are the Matsubara frequencies.

The f -level Green's function, without the renormalization factor, is given by:

$$\begin{aligned} F_{M_0 M_1; M_1 M_0}(i\omega_n) &= \frac{\Gamma_{M_0}}{2\pi i} \oint_C dz e^{-\beta z} \frac{1}{z(z+i\omega_n-\Delta)} \\ &= (P_{M_0} + P_{M_1})(i\omega_n - \Delta)^{-1} \end{aligned} \quad (13)$$

where the contour encloses all singularities,

$$\Delta = E_{M_1} - E_{M_0} \quad (14)$$

$$P_{M_i} = e^{-\beta E_{M_i}} / Z_0 \quad (15)$$

The renormalization factor

$$\left(1 - \frac{\partial Z(\beta)}{\partial \beta} \right)^{-1} \approx \frac{\Delta}{\Delta + T^2 N(E_F)} \quad (16)$$

contributes to the final result as a constant, we neglect it in the following calculations.

With the assumption of an isotropic hybridization matrix element

$$V_{\vec{k}}(\sigma M_0 M_1) V_{\vec{k}}^* (\sigma' M_1' M_0') V_{\vec{k}}^* (\sigma' M_1' M_0') V_{\vec{k}} (\sigma M_0 M_1) = V^4 \delta_{N_0 N_0'} \delta_{N_1 N_1'} \quad (17)$$

we perform the sum on ω_n :

$$c_{ij} = -\frac{V^4}{N_s^2} \sum_{N_0 N_1} (P_{M_0} + P_{M_1})^2 \sum_{\vec{k} \sigma} \sum_{\vec{k}' \sigma'} e^{i(\vec{k}-\vec{k}') \cdot \vec{R}_{ij}} \times \left\{ \frac{\beta^2 f_{\Delta}(1-f_{\Delta})}{(\epsilon_{\vec{k}\sigma}-\Delta)(\epsilon_{\vec{k}'\sigma'}-\Delta)} - \frac{2\beta f_{\Delta}}{(\epsilon_{\vec{k}\sigma}-\Delta)^2(\epsilon_{\vec{k}'\sigma'}-\Delta)} + \frac{2\beta f(\epsilon_{\vec{k}\sigma})}{(\epsilon_{\vec{k}\sigma}-\Delta)^2(\epsilon_{\vec{k}'\sigma'}-\epsilon_{\vec{k}\sigma})} \right\} \quad (18)$$

where $f(x) = (\exp(\beta x) + 1)^{-1}$ is the Fermi-Dirac distribution function.

Neglecting the Zeeman term of band electrons, the contribution of the two-site processes for the partition function is:

$$\sum_{ij} \tilde{S}_{ij} \approx \sum_{ij} c_{ij} = -\frac{2V^4}{N_s} \sum_{\vec{k} \neq 0} \sum_{N_0 N_1} (P_{M_0} + P_{M_1})^2 \sum_{\vec{k} \sigma} e^{i(\vec{k}-\vec{k}') \cdot \vec{R}} \times \left\{ \frac{\beta^2 f_{\Delta}(1-f_{\Delta})}{(\epsilon_{\vec{k}}-\Delta)(\epsilon_{\vec{k}'}-\Delta)} - \frac{2\beta f_{\Delta}}{(\epsilon_{\vec{k}}-\Delta)^2(\epsilon_{\vec{k}'}-\Delta)} + \frac{2\beta f(\epsilon_{\vec{k}})}{(\epsilon_{\vec{k}}-\Delta)^2(\epsilon_{\vec{k}'}-\epsilon_{\vec{k}})} \right\} \quad (19)$$

The free energy density owing to the intersite interaction is then the form:

$$f(R) = \frac{2V^4}{N_s} \sum_{N_0 N_1} (P_{M_0} + P_{M_1})^2 \sum_{\vec{k}} \sum_{\vec{k}'} e^{i(\vec{k}-\vec{k}') \cdot \vec{R}} \times \left\{ \frac{\beta f_{\Delta}(1-f_{\Delta})}{(\epsilon_{\vec{k}}-\Delta)(\epsilon_{\vec{k}'}-\Delta)} - \frac{2\beta f_{\Delta}}{(\epsilon_{\vec{k}}-\Delta)^2(\epsilon_{\vec{k}'}-\Delta)} + \frac{2f(\epsilon_{\vec{k}})}{(\epsilon_{\vec{k}}-\Delta)^2(\epsilon_{\vec{k}'}-\epsilon_{\vec{k}})} \right\} \quad (20)$$

The last term in the parenthesis of (20) represents a RKKY type of exchange interaction. In this process, the conduction electron interacts with f-electron at a site. Then the resulting electron-hole pair propagates to the other site and interacts once more with the f-system. This interaction dominates at the Zero-temperature limit:

$$f(R) \xrightarrow{T \rightarrow 0} -\frac{9N_s V^4}{16\mu^3} F\left(\frac{\Delta}{\mu}, \alpha\right) \quad (21)$$

where $\alpha = 2k_F R$ and

$$F\left(\frac{\Delta}{\mu}, \alpha\right) = -\frac{16\pi^3}{\alpha^2} \int_0^1 dx \frac{x \sin(\alpha x)}{[x^2 - (1 + \Delta/\mu)]^2} \quad (22)$$

If $2k_F R \Delta/\mu \gg 1$, then

$$f(R) = \frac{9\pi N_s V^4}{\mu \Delta^2} \frac{\cos \alpha}{\alpha^3} \quad (23)$$

we obtain the usual RKKY behavior.

If $2k_F R \Delta/\mu \ll 1$, then

$$f(R) = -\frac{9\pi N_s V^4}{\mu^2 \Delta} \frac{\sin \alpha}{\alpha^2} \quad (24)$$

Therefore in the mixed valence case ($2k_F R \Delta/\mu \ll 1$), the corresponding interaction is of longer range than the usual RKKY one. This result agrees with Tselik.⁵

At finite temperatures, the contributions of intersite interactions to the free energy can be evaluated with the aid of contour integrals. Starting from Eq.(20), we perform the \vec{k}' summation first. The result is:

$$f(R) = \frac{2V^4 V^4 k_F^2}{(2\pi)^3 N_s \mu R^2} \sum_{N_0 N_1} (P_{M_0} + P_{M_1})^2 \int_0^{2\pi} k dk \sin kR \times \left\{ \frac{\beta f_{\Delta}(1-f_{\Delta}) \cos k_F R}{\epsilon_{\vec{k}} - \Delta} - \frac{2f_{\Delta} \cos k_F R}{(\epsilon_{\vec{k}} - \Delta)^2} + \frac{2f(\epsilon_{\vec{k}}) \cos kR}{(\epsilon_{\vec{k}} - \Delta)^2} \right\} \quad (25)$$

where the following dispersion relation has been assumed:

$$\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m} - \mu$$

where μ is the chemical potential at $T=0K$.

Similar to the \vec{k}' summation, we next derive the \vec{k} summation. The contribution of second order poles at $\epsilon_{\vec{k}} = \Delta$ can be obtained by consider-

ing the last two terms altogether. Hence

$$f(R) = -\frac{9\pi^2 \gamma^4 N_s}{4\mu^2 \alpha^2} \sum_{N_0 N_1} (P_{N_0} + P_{N_1})^2 \times \left\{ \beta f_A (1-f_A) (1+\cos \alpha) + R k_F^2 f_A \sin \alpha / \mu \tilde{K}_F - G(\Delta, \mu, \alpha) \right\} \quad (27)$$

where

$$\tilde{K}_F = k_F (1 + \Delta/\mu)^{1/2}, \quad \alpha = 2\tilde{K}_F R \quad (28)$$

$$G(\Delta, \mu, \alpha) = \sum_{\omega_n} \exp[\alpha(i \operatorname{sgn}(\omega_n) - |\omega_n|/2\beta\mu)] (i\omega_n - \Delta)^{-2} = -\frac{\beta^2}{2\pi^2} \exp(-\pi\alpha/2\beta\mu) \operatorname{Re} \left[e^{i\alpha} \sum_{n=0}^{\infty} \frac{\exp(-n\pi\alpha/\beta\mu)}{(n+\frac{1}{2} + \beta\Delta/2\pi i)^2} \right] \quad (29)$$

As in Ref. 3, the last sum in (29) can be expressed in terms of the doubly generalized zeta-function, giving the temperature damping of the RKKY type of exchange interaction.

The first two terms in Eq. (27), contributed from the poles at $\tilde{E}_k = \Delta$, represent a superexchange interaction.⁸ In these processes, an electron is transferred from the conduction band into a singly occupied localized f orbital with different spin state because of the restrictions of Pauli exclusion principle. Then the generated hole in the conduction band interacts with the f electrons at another site. Finally the electron at the first site hops out of the doubly occupied f orbital. Thus the process is mediated from the first spin, by the opposite spin hole created in the conduction band, to the second site. This is an interaction peculiar to the mixed valence systems.

III. Calculations

In this section we discuss the contribution of two-site interactions to the susceptibility χ^{TS} . Before giving our calculation results, we

would like briefly conclude some features from the known experimental results.

Generally speaking, the behavior of the susceptibilities at high temperatures is easily understood by the Curie-Weiss law. For most of experimental curves, when temperature goes down to about 100K, a peak appears (maximum), then the curve bends down. And χ may show a minimum at low temperatures, making a trough in curve (see Fig. 3). Some of curves show another maximum at very low temperature.⁴ The first maximum can be explained by the on-site theory. But the nature of the low-temperature minimum (and maximum) still remains hidden.

For the purpose to explain the phenomena, we calculate χ^{TS} by taking the second derivative to free energy with respect to the magnetic field B.

$$\chi = \beta^{-1} \left. \frac{\partial^2 \ln Z}{\partial B^2} \right|_{B=0} = \chi^{\text{SS}} + \chi^{\text{TS}} + \dots \quad (30)$$

For a cubic lattice of mixed valence system, with the nearest neighbor approximation, we get

$$\begin{aligned} \chi^{\text{TS}} = & - \sum_{k_0} \left. \frac{\partial^2 f(R)}{\partial B^2} \right|_{B=0} = (9\pi^2 \gamma^4 N_s J(J+1)(2J+1) g^2 \mu_B^2 / 2\mu \alpha^2) \\ & \times \left\{ 2\beta^2 \left[\frac{V(1+2V)}{(1+(2J+1)V)^2} - \frac{V(1+V)}{(1+(2J+1)V)^2} \right] \cdot \right. \\ & \quad \times \left[f_A(1-f_A)(1+\cos \alpha) + R^2 k_F^2 \sin \alpha / \mu \tilde{K}_F + F_1 \right] \\ & \quad + 2\beta^2 \left[\frac{V(1+V)}{(1+(2J+1)V)^2} \right] \cdot \left[\beta f_A(1-f_A)(1-2f_A)(1+\cos \alpha) \right. \\ & \quad + \alpha f_A(1-f_A) k_F \sin \alpha / \mu \tilde{K}_F - R^2 k_F^2 f_A \sin \alpha / \beta \mu^2 \tilde{K}_F^2 \\ & \quad \left. \left. + R^2 k_F^4 f_A \sin \alpha / 2\beta \mu^3 \tilde{K}_F^3 + F_2 \right] \right. \\ & \quad \left. + \beta \left[\frac{(1+V)^2}{(1+(2J+1)V)^2} \right] \cdot \left[\beta^2 f_A(1-f_A)(-6f_A + 6f_A^2)(1+\cos \alpha) \right] \right\} \end{aligned}$$

$$\begin{aligned}
& + 3Rk_F^0 f_d(1-f_d)\sin\alpha/2\mu^2 k_F^3 - R^2 k_F^6 f_d \sin\alpha/\mu^2 k_F^3 \\
& - 3R^2 k_F^6 f_d \cos\alpha/2\mu^2 k_F^4 + 3Rk_F^6 f_d \sin\alpha/4\mu^2 k_F^5 \\
& + F_3 \} \quad (31)
\end{aligned}$$

where

$$\begin{aligned}
v &= e^{-\beta A} \\
F_1 &= \frac{1}{2\pi} \sum_{n=0}^{\infty} \exp(n\alpha/\beta\mu) [(n+\frac{1}{2})^2 + (\beta A/2\pi)^2]^{-2} \\
& \times \left\{ (n+\frac{1}{2})^2 - (\beta A/2\pi)^2 \right\} \cos\alpha + \beta A (n+\frac{1}{2}) \sin\alpha / \pi \} \\
F_2 &= \frac{\beta}{\pi^3} \sum_{n=0}^{\infty} \exp(n\alpha/\beta\mu) [(n+\frac{1}{2})^2 + (\beta A/2\pi)^2]^{-3} \\
& \times \left\{ \beta A [(n+\frac{1}{2})^2 - (\beta A/2\pi)^2] \cos\alpha / 2\pi + 2(\beta A/2\pi)^2 (n+\frac{1}{2}) \sin\alpha \right. \\
& \quad \left. + [(n+\frac{1}{2})^2 + (\beta A/2\pi)^2] \left(\frac{\beta A}{2\pi} \cos\alpha - (n+\frac{1}{2}) \sin\alpha \right) \right\} \\
F_3 &= \frac{\beta^2}{4\pi^4} \sum_{n=0}^{\infty} \exp(n\alpha/\beta\mu) \left\{ -\cos\alpha / [(n+\frac{1}{2})^2 + (\beta A/2\pi)^2]^2 \right. \\
& \quad \left. + \frac{12\beta A/2\pi}{[(n+\frac{1}{2})^2 + (\beta A/2\pi)^2]^3} \left\{ [(n+\frac{1}{2})^2 - (\beta A/2\pi)^2] \cos\alpha + \frac{\beta A}{\pi} (n+\frac{1}{2}) \sin\alpha \right\} \right. \\
& \quad \left. + \frac{2}{[(n+\frac{1}{2})^2 + (\beta A/2\pi)^2]^3} \left\{ 5\left(\frac{\beta A}{2\pi}\right)^2 \cos\alpha - (n+\frac{1}{2})^2 \cos\alpha - 4\frac{\beta A}{2\pi} (n+\frac{1}{2}) \sin\alpha \right\} \right\} \quad (32)
\end{aligned}$$

Through numerical calculations we have got a series of theoretical curves with different parameters. The four typical ones are shown in Fig. 4 a,b,c,d respectively. The contributions from the RKKY interaction and the superexchange interaction have been drawn separately. The superexchange interaction contributes to the susceptibility a single peak at $T \sim \Delta/3k_B$, while that of the RKKY interaction exhibit one or two peaks. The sign of χ^{TS} depends on the value of α and the order of magnitude of χ^{TS} has been found big enough to explain the minimum or maximum of low-temperature susceptibility.

It is clear from the computed peak and valley structures shown in Fig. 4a-d, in combination with on-site results, there may exist maximum or minimum in the susceptibility, as already observed in experiments. We found that the discrepancies between the experiments and the single site theory can be removed if the two-site contributions had been taken into consideration. For example, the satisfactory explanation of the low-temperature susceptibility of YbCuAl¹ can be achieved by adding the contribution of χ^{TS} with the type shown in Fig. 4c into the on-site results obtained by Bringer and Lustfeld.¹ We think that the peak and trough structures shown in Fig. 4a,4b and Fig. 4d may also corresponds to those observed in experiments⁴ if the variation of on-site contributions is flat at low temperatures. The direct comparison of the present theory with experiments can be made if the on-site contributions have also been calculated in the meantime. Unfortunately we have not made the calculation, but at least we have shown that the low-temperature susceptibility can be well-described by taking into consideration of intersite interactions.

IV. Discussions

This work is undertaken to get some insight into the nature of the intersite interactions in the mixed valence compounds. We have considered the contributions of the processes shown in Fig. 1 and Fig. 2. These processes, according to the viewpoint of $1/N$ expansion, are proportional to $1/N$, where $N=2J+1$. The more complicated two-site processes as shown in Fig. 5 and multisite processes as displayed in Fig. 6 are of higher order (N^{-2}, N^{-3}, \dots), therefore we neglect their contributions.

The consideration with these processes as well as the anisotropy of the hybridization matrix elements would be interesting for further studies.

The phenomena of the minimum of low-temperature susceptibility has been explained due to intersite interactions. We note that the low-temperature susceptibility of mixed valence compounds should exhibit a rich variety of behavior. Since the 1-dimension RKKY interactions in mixed valence compounds has been shown to be much stronger than that of 3-dimension,⁶ we expect the effects of intersite interactions would be stronger and interesting in the 1-dimension case.

It should be emphasized that the minimum susceptibility is only a specific example showing the importance of the intersite interactions. We have noted that in many other thermodynamic and transport properties there also exist some interesting phenomena in mixed valence compounds. We believe that considering the effects of intersite interactions should be conducive to understand these phenomena. Although our main concern has been the susceptibility of intersite interaction, it should be straightforward to calculate other thermodynamic quantities from the expressions for the general formula of partition function given in this paper.

It should be emphasized once more that the intersite interactions in mixed-valent compounds is much stronger than that in non-mixed valent materials since the conduction electrons which propagate between different sites can carry and transmit more information due to the hybridization processes. Even in the case $T \ll T_K$, where T_K is the Kondo temperature, the RKKY interaction is still exist.⁶ Although under the condition the

ion magnetic moment is screened by electron cloud in average, owing to the loose structure of the cloud, the magnetic ions in the neighborhood are still affected by the RKKY interaction. The T_K has found to be decreased by the RKKY interaction as well.⁶ In other words, the RKKY interaction will influence the spin-flip processes.

It is worth noting that the recent experimental curves of χ for samples $ZrIr_2$ and $ZrOs_2$ with impurities Pr also show the similar behavior as our theoretical curves: Fig.4b and Fig.4d. Our theory is available for the case of impurities and thus the above mentioned experimental phenomena can be interpreted by our present theory.

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Figure Captions

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Fig. 1 Indirect interactions between the f electrons at different sites via band electrons.

Fig. 2 Renormalized indirect interaction between the f electrons at different sites via band electrons.

Fig. 3 Experimental susceptibility curves.(Reproduced from Ref. 4)

Fig. 4 The temperature dependences of susceptibility coming from contributions of intersite interaction. The solid line is the contribution of RKKY. The dashed line is the contribution of superexchange interaction. The dotted-dashed line is the contribution of combination of RKKY and superexchange interactions. The parameters used in calculations are the following:

Fig. 4a $\alpha = 13.0$; $\Delta/k_B = 20K$; $\mu = 2eV$; $J = 7/2$; $T/k_B = 100K$

Fig. 4b $\alpha = 12.5$; $\Delta/k_B = 30K$; $\mu = 5eV$; $J = 7/2$; $T/k_B = 80K$

Fig. 4c $\alpha = 20.0$; $\Delta/k_B = 10K$; $\mu = 5eV$; $J = 5/2$; $T/k_B = 80K$

Fig. 4d $\alpha = 15.0$; $\Delta/k_B = 30K$; $\mu = 5eV$; $J = 5/2$; $T/k_B = 150K$

Fig. 5 Diagrams representing more complicated two-site processes which is of higher order than $1/N$.

Fig. 6 Diagrams representing multisite processes which is of higher order than $1/N$.

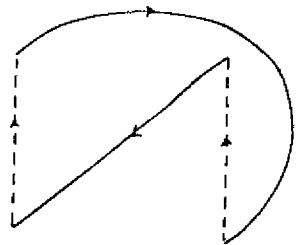


Fig. 1

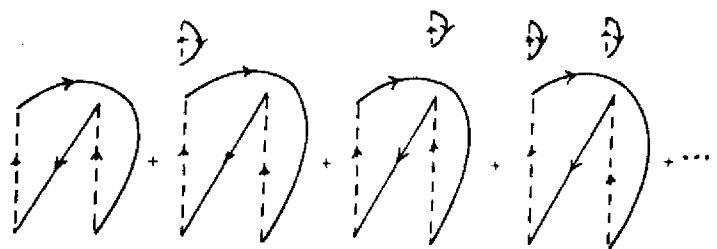


Fig. 2

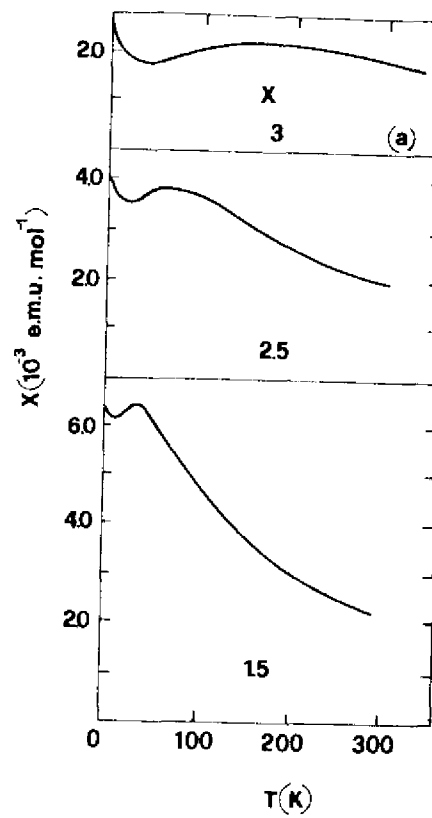


Fig. 3

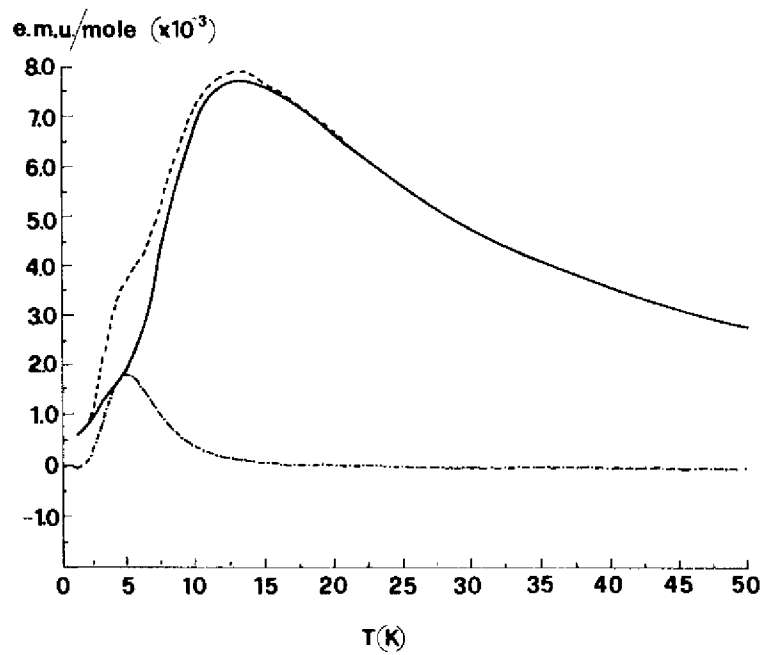


Fig. 4 (a)

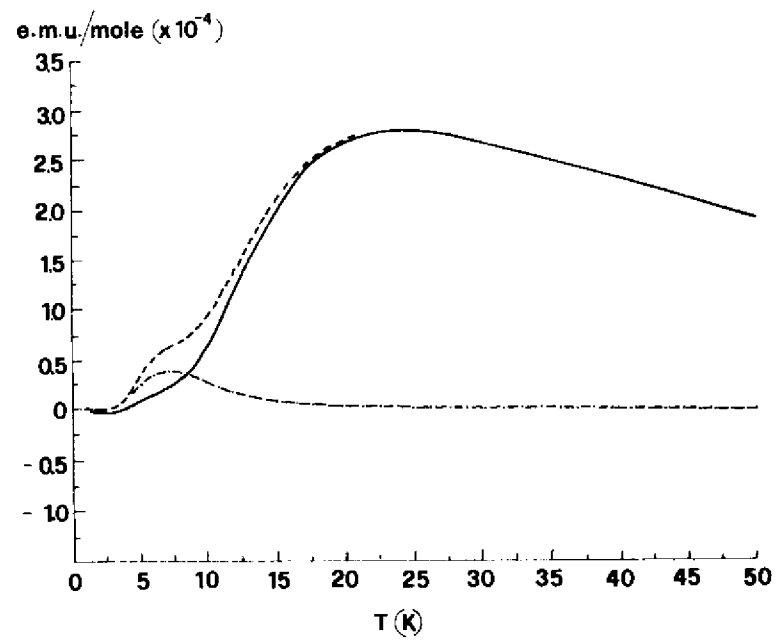


Fig. 4 (b)

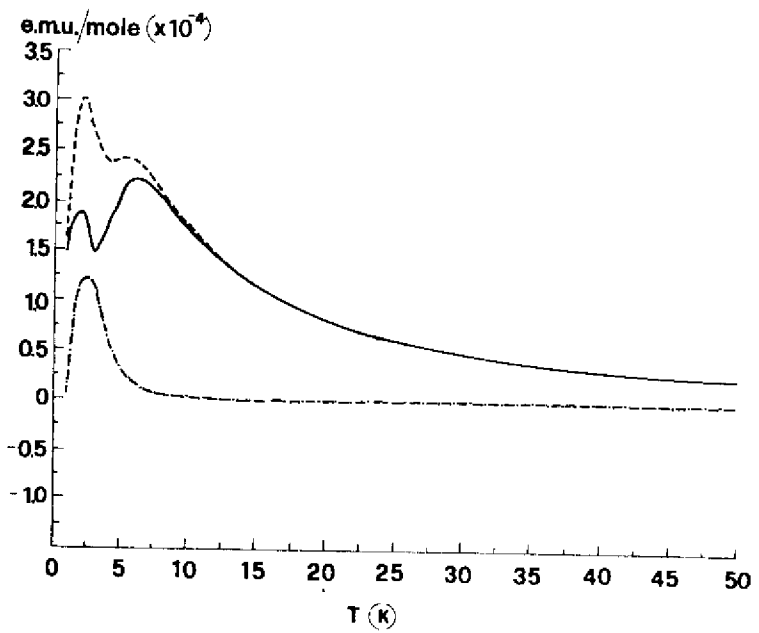


Fig. 4 (c)

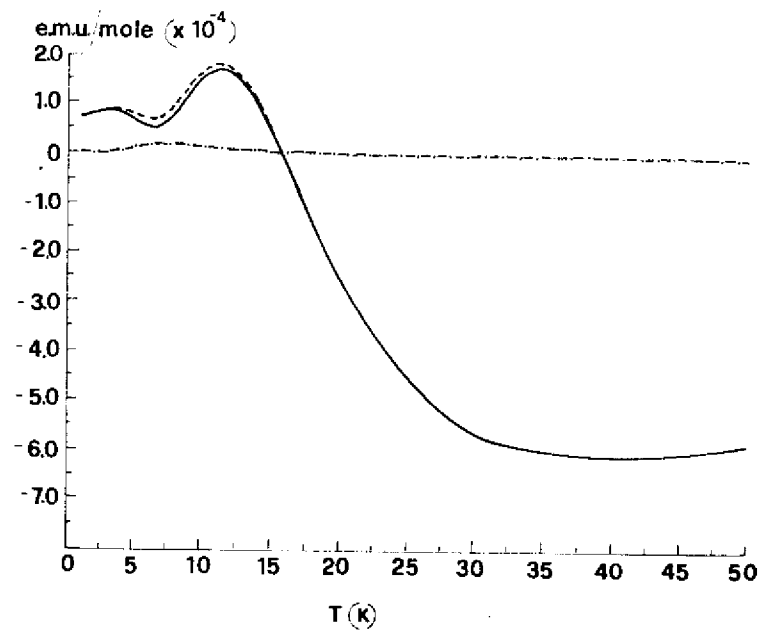


Fig 4 (d)

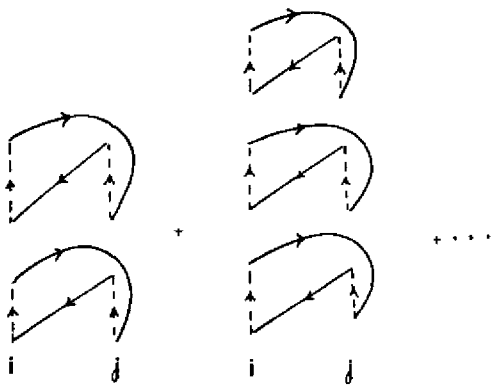


Fig. 5

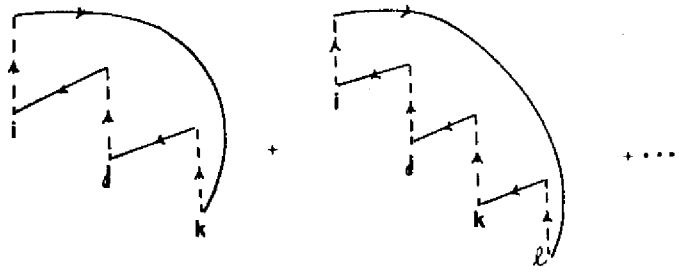


Fig. 6